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13. ABSTRACT (Maximum 200 words) This project has involved the design of new inorganic/organic/organometallic polymers and the development of new methodologies that allow their synthesis. The new polymers have properties that range from elastomers or membranes to glasses to electroactive materials, and are expected to be useful in a range of applications that require low-temperature flexibility, resistance to hydrocarbons, oxidation-resistance, and sensor behavior.					
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THE SYNTHESIS AND STRUCTURE OF POLYPHOSPHAZENES

FINAL REPORT FOR PERIOD JUNE 15, 1988 - JUNE 14, 1991

U .S. Army Research Office

DAAL03-88-K-0112
25280-CH

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PROBLEM STUDIED

The purpose of this work was the design, synthesis, and property evaluation of new polymers derived from the inorganic elements. A major component of the work was the development of synthesis methodologies that would allow access to new polymer systems, and a relating of properties to polymer structure in ways that would permit effective molecular design in future work.

SUMMARY OF THE MOST IMPORTANT RESULTS

New polyphosphazenes have been synthesized that bear cyano, isothiocyano, ferrocenyl, η^6 -arene chromium carbonyl, and phosphazo side groups. The properties of these polymers range from elastomers to electroactive or photoactive polymers. The isothiocyanato polymers are reactive intermediates for preparation of a broad range of new inorganic organic-substituted polymers including bioactive species.

Two methods have been discovered for facilitating the ring-opening polymerization of cyclic phosphazenes to high polymers. The first involves the introduction of ring strain by incorporation of trans-annular ferrocene units. Some of these trimers polymerize directly to fully organo-substituted phosphazene high polymers without the need for a subsequent macromolecular substitution step. The second method involves the use of cyclic molecules that contain carbon or sulfur in the ring, along with phosphorus and nitrogen. The resultant poly(carbophosphazenes) and poly(thiophosphazenes) are the first members of new classes of inorganic polymers with properties that extend those found in classical polyphosphazenes.

The development of relationships between molecular structure, and polymerization behavior or polymer properties has been accomplished by X-ray diffraction and molecular mechanics studies of a broad range of small-molecule cyclic and linear phosphazenes with different side groups and by X-ray studies on the corresponding high polymers. These studies provide the raw material needed to design polymers for specific advanced engineering uses.

PUBLICATIONS

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I. Manners, G. H. Riding, J. A. Dodge, and H. R. Allcock*
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I. Manners, G. Renner, O. Nuyken, and H. R. Allcock*
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H. R. Allcock
Solid State Ionics **1989**, 32/33, 761-764.

"Transition Metal Derivatives of Phosphinophosphazenes: X-ray Crystal Structures of

$\text{N}_3\text{P}_3\text{Cl}_4\text{PhPPh}_2$, $\text{N}_3\text{P}_3\text{Cl}_4\text{PhPPh}_2\cdot\text{Cr}(\text{CO})_5$, and $\text{N}_3\text{P}_3\text{Cl}_4\text{PhPPh}_2\cdot\text{Ru}_3(\text{CO})_{11}$
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"Poly[(aryloxy)carbophosphazenes]: Synthesis, Properties, and Thermal Transition Behavior"

H. R. Allcock,*, S. M. Coley, I. Manners, O. Nuyken and G. Renner
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"Syntheses and Structures of Cyclic and Short-Chain Linear Phosphazenes Bearing 4-Phenylphenoxy Side Groups"

H. R. Allcock*, D. C. Ngo, M. Parvez, and R. R. Whittle (The Pennsylvania State University), and W. J. Birdsall (Albright College)
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H. R. Allcock*, J. S. Rutt, and M. Parvez
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"Synthesis and Structure of Phosphazene (η^6 -Arene)chromium Tricarbonyl Derivatives"

H. R. Allcock*, A. A. Dembek, J. L. Bennett, I. Manners, and M. Parvez
Organometallics **1991**, 10, 1865-1874.

"Poly(phosphazophosphazenes): A New Class of Inorganic Polymers with Short-Chain Branching"

D. C. Ngo, J. S. Rutt, and H. R. Allcock*
J. Am. Chem. Soc. **1991**, 113, 5075-5076.

"Synthesis, Reactivity, and the Electronic Structures of Fluoro- and Hydrido-Phosphazene Anions: X-ray Crystal Structure of $[Li(THF)_3][N_3P_3F_2H(BEt_3)(\eta-C_5H_4)_2Fe]$ "

H. R. Allcock*, W. D. Coggio, I. Manners, and M. Parvez
Organometallics (in press)
(abstract included in last progress report)

"Cyclic and High Polymeric Cyanophosphazenes: Synthesis and X-ray Structural Characterization"

H. R. Allcock*, J. S. Rutt, M. F. Welker, and M. Parvez
Inorganic Chemistry (in press)
(abstract included in last progress report).

"Synthesis of Strained Ferrocenylorganocyclophosphazenes: X-ray Crystal Structures of $N_3P_3(OCH_2CF_3)_4(\eta-C_5H_4)_2Fe$, $N_3P_3(OPh)_4(\eta-C_5H_4)_2Fe$, and $N_3P_3Ph_2(OCH_2CF_3)_2(\eta-C_5H_4)_2Fe$ "

H. R. Allcock*, J. A. Dodge, I. Manners, M. Parvez, G. H. Riding, and K. B. Visscher

Organometallics (in press)
(abstract included in last progress report).

"Synthesis and Structures of Para-Halogenophenoxy Phosphazenes: A Comparison of the Structures of Cyclic and Linear Short Chain Species"

H. R. Allcock,* D. C. Ngo, M. Parvez, and K. B. Visscher

Inorganic Chemistry (in press)
(abstract included in last progress report).

"Synthesis and Characterization of Polyphosphazene (η^6 -Arene)chromium Tricarbonyl Derivatives"

H. R. Allcock,* A. A. Dembek, and E. H. Klingenberg

Macromolecules (in press)

Abstract: The synthesis and structure of a new class of poly(metallophosphazenes) is described. The polymers have the general formulas $[\text{NP}(\text{OR})_2]_n$ and $[\text{NP}(\text{OR})_x(\text{OCH}_2\text{CF}_3)_y]_n$, where the OR side group is 2-phenoxyethoxy chromium tricarbonyl, and $x + y = 100\%$. The single-substituent polymer is the first example of a poly(metallophosphazene) which has one transition metal unit on every side group. Non-metallo polymers with the general structures $[\text{NP}(\text{OR}')_2]_n$, $[\text{NP}(\text{OR}')_2]_n(\text{OCH}_2\text{CF}_3)_y]_n$, and $[\text{NP}(\text{OCH}_2\text{CF}_3)_2]_n$, where the OR' substituent is 2-phenoxyethoxy, and $x + y = 100\%$, were prepared for comparison with the corresponding metallocene polymers. Structural characterization for the high polymers was carried out by NMR spectroscopy, infrared spectroscopy, gel permeation chromatography, and elemental analysis. Thermal analysis of the polymers was investigated by differential scanning calorimetry and thermogravimetric analysis.

"Strain-Induced Ring-Opening Polymerization of Ferrocenyl-organocyclotriphosphazenes: A New Route to Poly(organophosphazenes)"

H. R. Allcock,* Jeffrey A. Dodge, Ian Manners, and G. H. Riding

Journal of the American Chemical Society (in press)

Abstract: The strained transannular ferrocenylcyclotriphosphazenes $\text{N}_3\text{P}_3(\text{OCH}_2\text{CF}_3)_4(\eta\text{-C}_5\text{H}_4)_2\text{Fe}$, $\text{N}_3\text{P}_3\text{R}(\text{OCH}_2\text{CF}_3)_3(\eta\text{-C}_5\text{H}_4)_2\text{Fe}$, [$\text{R} = \text{OPh}$, $\text{R} = \text{Me}$, $\text{R} = \text{Ph}$ (R gem to Cp), and $\text{R} = \text{Ph}$ (non-gem to Cp)], and $\text{N}_3\text{P}_3\text{R}_2(\text{OCH}_2\text{CF}_3)_2(\eta\text{-C}_5\text{H}_4)_2\text{Fe}$ (gem to Cp) and $\text{R} = \text{Ph}$ (non-gem to Cp)] undergo ring-opening polymerization when heated at 250°C in the presence of a small amount (1%) of $[\text{N}(\text{PCl}_2)_3]$, which functions as a polymerization initiator. The cyclic trimers $\text{N}_3\text{P}_3(\text{OPh})(\text{OCH}_2\text{CF}_3)_3(\eta\text{-C}_5\text{H}_4)_2\text{Fe}$, $\text{N}_3\text{P}_3\text{Me}(\text{OCH}_2\text{CF}_3)_3(\eta\text{-C}_5\text{H}_4)_2\text{Fe}$, and $\text{N}_3\text{P}_3\text{Ph}_2(\text{OCH}_2\text{CF}_3)_2(\eta\text{-C}_5\text{H}_4)_2\text{Fe}$ (Ph groups non-gem to Cp) also polymerize at 250°C , but in the absence of $[\text{N}(\text{PCl}_2)_3]$. These transformations are the first examples of uncatalyzed ring-opening polymerization of cyclic phosphazenes that lack phosphorus-halogen bonds. By contrast, the sterically-crowded cyclotriphosphazene $\text{N}_3\text{P}_3(\text{OPh})_4(\eta\text{-C}_5\text{H}_4)_2\text{Fe}$ undergoes ring expansion to the corresponding cyclic hexamer when heated at 250°C in the presence or absence of $[\text{N}(\text{PCl}_2)_3]$, but it does not polymerize. When heated in the absence of $[\text{N}(\text{PCl}_2)_3]$, $\text{N}_3\text{P}_3(\text{OCH}_2\text{CF}_3)_4(\eta\text{-C}_5\text{H}_4)_2\text{Fe}$, $\text{N}_3\text{P}_3(\text{OPh})(\text{OCH}_2\text{CF}_3)_3(\eta\text{-C}_5\text{H}_4)_2\text{Fe}$, and $\text{N}_3\text{P}_3\text{Ph}(\text{OCH}_2\text{CF}_3)_3(\eta\text{-C}_5\text{H}_4)_2\text{Fe}$ (Ph non-gem to Cp) also undergo ring expansion to form the corresponding cyclic hexamers. The Lewis acid BCl_3 initiates the ring-opening polymerization of $\text{N}_3\text{P}_3(\text{OCH}_2\text{CF}_3)_4(\eta\text{-C}_5\text{H}_4)_2\text{Fe}$ and catalyzes the ring-expansion of $\text{N}_3\text{P}_3(\text{OPh})_4(\eta\text{-C}_5\text{H}_4)_2\text{Fe}$.

Possible explanations for the differences in thermal behavior are given. The implications of these results for the mechanisms of phosphazene ring-opening polymerization and ring-ring equilibration are also discussed.

PERSONNEL

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Masood Parvez (Department X-ray Crystallographer)
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Eric Silverberg (Graduate Student)
Gerhard Renner (Ph.D. student on leave from Professor O. Nuyken's group at the University of Bayreuth, West Germany; 90% of his stipend was provided by Bayer AG Company)

INVENTIONS

"The Syntheses of Poly(chlorophosphazophosphazene) and Poly(organophosphazophosphazene) via Thermal Ring-Opening Polymerization of Bis(trichlorophosphazo)-tetrachlorocyclotriphosphazene"

"Polycarbophosphazenes: A New Class of Inorganic-Organic Macromolecules"

"Polythiophosphazenes: New Inorganic Macromolecules with Backbones Composed of Phosphorus, Nitrogen, and Sulfur Atoms"